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SYNTHESIS AND STRUCTURAL CHEMISTRY OF Au(III)-SUBSTITUTED $Ba_2YCu_3O_{7-\delta}$

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ABSTRACT

Gold-substituted superconductors, $Ba_2Y(Au_xCu_{1-x})_3O_{7-\delta}$ (x = 0 - 0.1) have been synthesized. For x = 0.1, there is no change in the a and b lattice parameters (a = 3.826 Å and b = 3.889 Å) but a 0.06 Å c axis expansion to 11.75 Å is observed. Substituted gold is found to be trivalent by XPS. Replacing Cu(1) in the copper oxide chain with a slight reordering of oxygen is consistent with c axis expansion. The formal charge of the site remains trivalent; remaining Cu in the chains may be reduced resulting in an oxygen stoichiometry ≤ 7. A small effect on T_c (89 K for x = 0.10) is observed upon gold substitution.

INTRODUCTION

Since reports of the synthesis[1] and structure[2] of the superconductor $Ba_2YCu_3O_{7-\delta}$, many copper substitution studies have appeared. These efforts have mainly focused on ions of the first row transition[3-6] and Group IIIB[5-7] metals. Typically, trivalent ions substitute at the Cu(1) site in copper oxide chains and induce an orthorhombic/tetragonal transition while divalent ions substitute in copper oxide planes and do not cause a major structural shift. Oxygen ordering is disrupted by the structural requirements of substituting ions, lowering T_c, particularly for Cu(2) substitution (e.g. Zn^{2+}).[3]

An understanding of the structural and superconducting properties of metal doped perovskite superconductors is critical not only for possible insights into mechanisms of ceramic superconductivity but also because these phases are often formed during synthesis of useful superconducting structures (i.e. thin films[7] or composites[8]). We present results on the formation and properties of Au(III)-substituted $Ba_2YCu_3O_{7-\delta}$. We discuss these results as they relate to the chemistry of Au(III) and the use of gold-containing superconducting materials.

EXPERIMENTAL

The superconducting oxides were synthesized from CuO, BaO_2, Y_2O_3, and Au_2O_3 powders ground together and fired at 950°C for 32 hours. BaO_2 was used to prevent gold reduction; it was also used to optimize doping homogeneity. This is shown in figure 1 for an undoped superconductor and discussed elsewhere.[9] XPS measurements were made on a Perkin-Elmer XPS-AES-SIMS instrument. A. C. susceptibility and d. c. resistance were used to measure T_c. X-ray powder data were collected on a diffractometer using monochromated Cu K_α radiation.

RESULTS

Structural data for a series of $Ba_2Y(Au_xCu_{1-x})_3O_{7-\delta}$ superconductors is shown in figure 2. The assignment of the trivalent oxidation state is made by virtue of XPS data which shows a shoulder at 87 eV. This 3 eV shift from metallic gold is characteristic of the trivalent state.[10] Maintenance of the integrity of the a-b plane and expansion of the c axis is the most striking result of our study. These results stand in stark contrast to earlier results with trivalent metal ion substitution which produces a tetragonal structure for Fe,[4,6] Co,[4,6] Al,[6,7] and Ga[5] for $x < 0.10$. An interesting illustration of the lengthening of the c axis is shown in figure 3. As the mole percent of Au(III) is increased from x = 0 to 0.05 and then to 0.10, the 006 peak in the x-ray pattern shifts to lower 2θ values while the 020 and 200 peaks remain stationary. This destroys the coincidence between the 006 and 020 peaks in the x-ray pattern of the native structure.

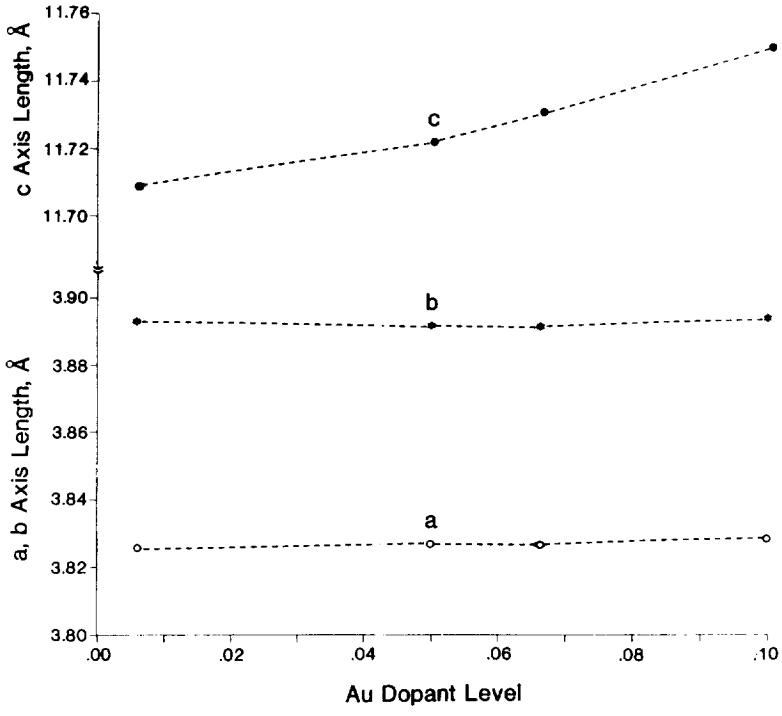

FIG 2. Lattice constants of Au (III)-substituted $Ba_2YCu_3O_{7-\delta}$ vs. Au (III) substitution level. Note that while a and b axes remain constant, c axis expands 0.06 Å. See text for discussion.

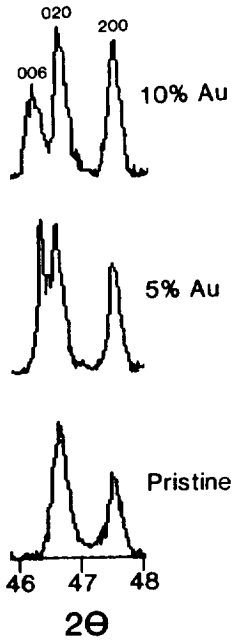

FIG. 3. XRD data for Au (III)-substituted $Ba_2YCu_3O_{7-\delta}$.

DISCUSSION

Structural considerations have been mentioned by several groups as leading to oxygen disordering. For example, substitution of Al^{3+}, which prefers octahedral coordination eventually drives the structure tetragonal to achieve a more stable Al coordination environment,[7] the same argument would also apply to Ga^{3+}.[5] Fe^{3+} and Co^{3+} prefer tetrahedral or octahedral and octahedral coordination, respectively and have been noted to cause similar disordering.[4] The differing effects of Ni^{2+} and Zn^{2+} may be in the increased tolerance of d^8 ions for square pyramidal coordination as opposed to d^{10} Zn^{2+} which tends towards tetrahedral coordination to minimize ligand repulsion.

With these considerations in mind, the influence of Au(III) is consistent with the observed substitution chemistry of perovskite superconductors and the chemistry of trivalent gold. Au(III) is known to form square planar complexes almost exclusively due to the large difference in energy between the unfilled $d_{x^2-y^2}$ and the filled d_{z^2} orbitals of the $5d^8$ ion. The expansion of the c axis can be attributed to the larger size of the Au(III) in the same way that a slight decrease in the c axis was noted for Al substitution.[7] However, we did not observe an increase of the b axis which would be expected for simple substitution at the Cu(1) site.

We believe there is a slight reordering of oxygen involving the a-b plane accompanied by reduction of the other Cu ions to Cu(I). More detailed studies are in progress to elucidate the exact nature of the oxygen ordering at the Au(III) site. We also considered Au(III) doping at the rare earth site or simply not substituting into the lattice. However, neither result is consistent with a slight decrease in oxygen stoichiometry (*vide infra*) or the lack of a second phase such as Y_2BaCuO_5[11] expected due to our reaction stoichiometries.

Reduction of Cu(1) on the chain to Cu(I) has also been observed to increase the c lattice parameter.[6] In fact it has been noted that trivalent doping may be accompanied by either oxygen increase or reduction of Cu on the chain to Cu(I).[4,6] Our crude weight loss results from reaction data indicate a slight decrease in oxygen stoichiometry. These results can be contrasted to other trivalent metal ion substitutions which exhibit oxygen stoichiometries ≥ 7 for Co,[4,6] Fe,[4,6] Ga,[5] or Al.[6,7] It is interesting to note that Zn doping may actually lead to a slight decrease in oxygen which correlates to Zn concentration ($\delta = 0.3$ when $x = 0.3$) and to the preferred tetrahedral coordination of Zn^{2+}.[6] Substitution of Au(III) leads to formation of two coordinate Cu(I) which may result in a slight loss of oxygen along the chains.

Data from other substitution studies indicate that doping in the a-b plane has a greater impact on superconductivity than doping on the chains.[3-7] The impact of trivalent metal ion doping arises when the electronic configuration of the substituting ions induces a structural change, an oxygen disordering and influences the structure of Cu(II)

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